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REPORT

Evaluation of annual resolution coral geochemical records as climate proxies in the Great Barrier Reef of Australia

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Abstract Sampling of annually banded massive coral skeletons at annual (or higher) resolutions is increasingly being used to obtain replicate long-term time series of changing seawater conditions. However, few of these studies have compared and calibrated the lower annual resolution records based on coral geochemical tracers with the corresponding instrumental climate records, although some studies have inferred the climatic significance of annual coral series derived from averages of monthly or sub-annual records. Here, we present annual resolution analysis of coral records of elemental and stable isotopic composition that are approximately 70 years long. These records were preserved in two coexisting colonies of *Porites* sp. from Arlington Reef, on the Great Barrier Reef in Australia, and are used to evaluate the climatic significance of annually resolved coral geochemical proxies. The geochemical records of coral sample "10AR2," with its faster and relatively constant annual growth rate, appear to have been independent of skeletal growth rate and other vital effects. The annual resolution of Sr/Ca and $\Delta\delta^{18}O$ time series was shown to be a good proxy for annual sea surface temperature (SST; $r = -0.67$, $n = 73$, $p < 0.0000001$) and rainfall records ($r = -0.34$, $n = 67$, $p < 0.01$). However, a slower growing coral sample, "10AR1" showed significantly lower correlations ($r = -0.20$, $n = 71$, $p = 0.05$ for Sr/Ca and SST; $r = -0.19$, $n = 67$, $p = 0.06$ for $\Delta\delta^{18}O$ and rainfall), indicating its greater susceptibility to biological/metabolic effects. Our results suggest that while annually resolved coral records are potentially a valuable tool for determining, in particular, long timescale climate variability such as Pacific Decadal Oscillation, Interdecadal Pacific Oscillation, and other climatic factors, the selection of the coral sample is important, and replication is essential.

Keywords Coral · Sr/Ca · Mg/Ca · Carbon and oxygen isotopes · Great Barrier Reef

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Introduction

Geochemical records, such as isotopic compositions ($\delta^{18}O$, $\delta^{13}C$, etc.) and elemental ratios (Sr/Ca, Mg/Ca, U/Ca, etc.), obtained from massive reef-building corals can provide high-resolution records of past climatic conditions over timescales ranging from weekly to seasonal to annual as well as decades to centuries (Gagan et al. 2000; Cole 2003; Felis and Pätzold 2003). To acquire seasonal to monthly climatic information, most studies sample coral skeletons at very high-resolution intervals (ca. 1 mm or less; e.g., McCulloch et al. 1994; Alibert and McCulloch 1997; Gagan et al. 1998; McCulloch et al. 1999; Sun et al. 2004; Wei et al. 2007; Deng et al. 2009; Duprey et al. 2012; DeLong et al. 2013). However, high-resolution sampling requires a considerable number of subsamples for analysis, which makes coral-based climate reconstructions time consuming, labor intensive, and expensive. Although the development of laser ablation analytical techniques has made high-resolution elemental ratio analysis faster and more convenient than traditional wet chemical methods (Sinclair et al. 1998; Fallon et al. 1999; McCulloch et al. 2003; Deng et al. 2010), the analytical precision of the laser ablation method remains generally poor relative to that expected from, for example, changes in seawater temperature. For many isotopic proxies, especially the non-traditional isotope systems such as magnesium, calcium, boron, and clumped isotopes, a series of complex chemical separation and purification procedures are needed, and these procedures remain burdensome (Pelejero et al. 2005; Böhm et al. 2006; Ghosh et al. 2006; Wei et al. 2009; Yoshimura et al. 2011). Consequently, the high-resolution analysis of these geochemical systems is generally not practical, especially over multi-decadal timescales.

As the currently available techniques and methods often make high-resolution analytical work using long time series impractical, the use of relatively low-resolution annual sampling offers an alternative strategy that provides both the larger sample sizes necessary for the application of some proxies (e.g., boron isotopes), as well as facilitating longer timescale, coral-based climate reconstruction studies. In particular, for the study of decadal or interdecadal climate variability, such as the Pacific Decadal Oscillation (PDO), and the Interdecadal Pacific Oscillation (IPO), relatively low-resolution sampling is preferable. Nevertheless, relative to the large quantity of high-resolution studies, annual to multi-year resolution coral-based studies are still relatively rare. In addition, of those coral-based studies undertaken at annual to pent-annual resolutions (Dunbar et al. 1994; Cole et al. 2000; Hendy et al. 2002; Pelejero et al. 2005; Calvo et al. 2007; Linsley et al. 2008; Abram et al. 2009; Wei et al. 2009; Deng et al. 2013; Zinke et al. 2014), few have focused on the replication of the low-resolution geochemical records of multiple coral cores. Some studies have evaluated the climatic significance of annual coral records averaged using monthly or sub-annual values from each year (Lough 2004; Smith et al. 2006; Pfeiffer et al. 2009). However, such approaches may suffer from biases caused by the attenuation of the coral geochemical records, which leads to an overestimate of the changes in sea surface temperature (SST) over decadal to millennial timescales (Gagan et al. 2012).

The regression slope relations of coral $\delta^{18}O$–SST calibration on monthly and annual timescales are different (Crowley et al. 1999); therefore, the response of coral geochemistry to climatic and environmental factors, such as SST, may be different at a seasonal resolution to that at annual to pent-annual resolutions. The best way to evaluate the applicability of geochemical records based on a low sampling resolution may be to calibrate them with the corresponding instrumental data and to check the replication of at least two or three corals, as performed in high-resolution sampling studies (Lough 2004; DeLong et al. 2013). This approach could test whether low-resolution sampling accurately records climatic and environmental changes, and also derive the quantitative relationship between geochemical parameters obtained from low-resolution sampling, and climatic and environmental factors. With this in mind, we report here geochemical time series based on the annual sampling of two *Porites* sp. coral heads drilled at Arlington Reef, which is located on the Great Barrier Reef (GBR), Australia, to assess the degree of agreement between the geochemical records preserved within these two corals. We also describe the relationships between the annual resolution coral geochemical proxies and the corresponding instrumental climate records. This may help to evaluate whether the geochemical variations in these annual records accurately reflect climatic variability, enabling the more widespread application of paleoclimatic reconstructions based on annual resolution geochemical records.

Materials and methods

Coral sampling

In April 2010, two long cores with a diameter of 6 cm, referred to herein as 10AR1 (1.03 m length) and 10AR2 (1.24 m length), were drilled using underwater drilling techniques from two separate, living, *Porites* sp. coral colonies that were approximately 50 m apart on Arlington Reef, immediately offshore from Cairns on the northeast coast of Australia (Fig. 1). These coral cores were cut lengthwise into slabs 7 mm thick and X-rayed to reveal regular and well-defined annual density bands that were then used to establish the coral chronology (10AR1: 1939–2009; 10AR2: 1937–2009) and obtain information regarding the coral's annual growth rates (Fig. 2). The annual growth rate was directly measured along the major growth axis from the X-rayed photograph as the length of each annual density band comprising of a high- and low-density band, with a precision of 1 mm. The high-density bands were assigned to winter and low density to summer. The slabs were ultrasonically cleaned in water purified by the Millipore system (Milli-Q water), rinsed three times, and dried at 40 °C prior to sampling. Before collecting the samples, preliminary milling along the designated sample track was undertaken to remove approximately the upper 1 mm. Guided by the annual bands identified in the X-rays, samples (ca. 1 g) were collected at annual intervals from sampling grooves around 1 cm wide along the main growth

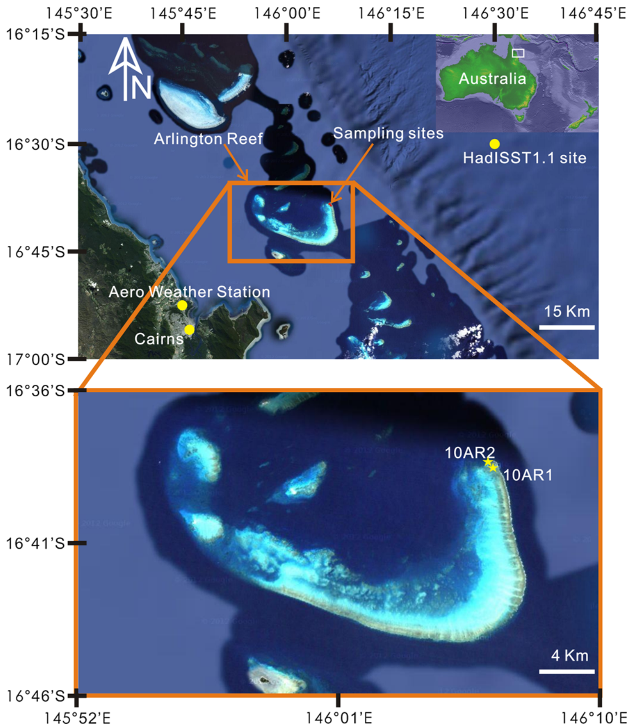

Fig. 1 Map showing the location of Arlington Reef on the Great Barrier Reef (GBR). *Inset* shows location of the GBR in Northern Queensland. The *stars* indicate the sample locations

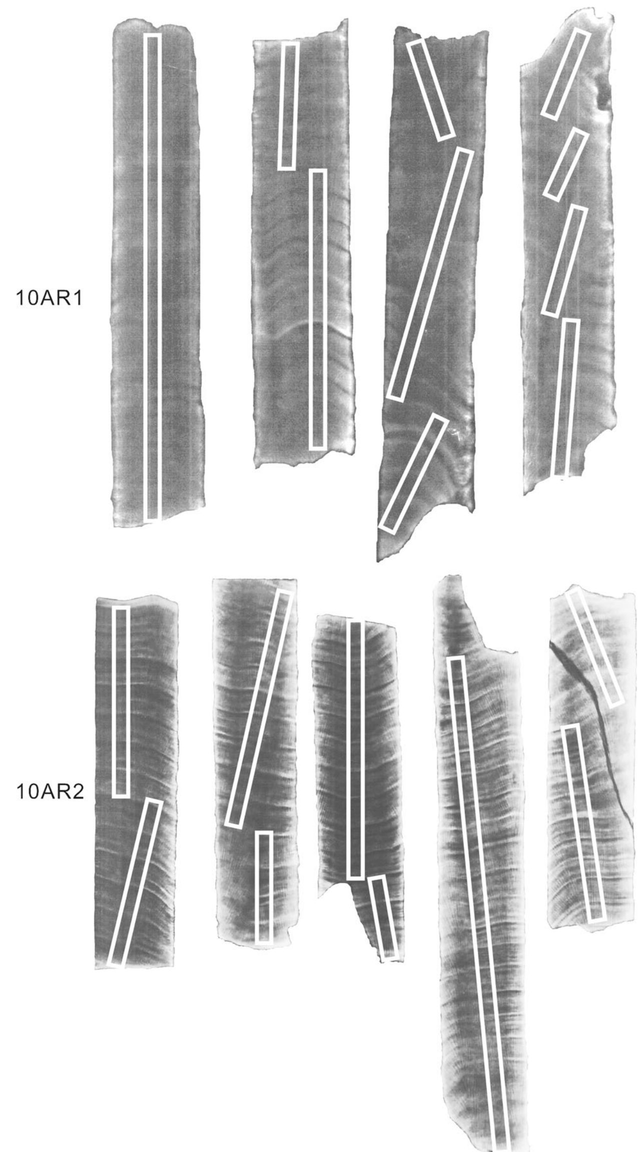

Fig. 2 X-radiographs (negative images) of the two *Porites* sp. corals 10AR1 (*upper panel*) and 10AR2 (*lower panel*) collected from Arlington Reef. The *rectangles* indicate the location of the sampling grooves

axis using a semi-automated milling machine, then ground into a fine powder (ca. 200 mesh) using an agate mortar and pestle. Stable isotope and elemental ratios were then obtained for each annual sample.

Geochemical analysis

Coral skeletal $\delta^{13}C$ and $\delta^{18}O$ measurements were performed at the State Key Laboratory of Isotope Geochemistry (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences) on a GV Isoprime II stable isotope ratio mass spectrometer (IRMS) coupled with a MultiPrep® carbonate device that used 102 % H_3PO_4 at 90 °C to extract CO_2 from the annual resolution coral samples (ca. 0.2 mg) and following the procedures described by Deng et al. (2009). Isotope data were normalized to the Vienna Pee Dee Belemnite (V-PDB) using the NBS-19 standard ($\delta^{13}C = 1.95$ ‰, $\delta^{18}O = -2.20$ ‰). Multiple measurements ($n = 30$) of this standard yielded a standard deviation of 0.05 ‰ for $\delta^{13}C$, and 0.08 ‰ for $\delta^{18}O$. Replicate measurements were made on approximately 15 % of the samples, and the differences between the results of the repeated measurements were within the range of analytical errors.

Sr/Ca and Mg/Ca analysis of annual samples (ca. 1 mg) was carried out on a Varian Vista Pro inductively coupled plasma atomic emission spectrometer (ICP-AES) at the same laboratory. Replicate analysis of an in-house coral standard solution showed excellent reproducibility, with an external precision of 0.16 % for Sr/Ca and 0.3 % for Mg/Ca. About 15 % of the samples were repeated, and the differences between the results of the repeated measurements were also within the range of analytical error. See Wei et al. (2007) for a more detailed description of the methodology.

Residual $\delta^{18}O$ ($\Delta\delta^{18}O$), a coral proxy for changes in the $\delta^{18}O$ levels in the surrounding seawater, was calculated by subtracting the SST contribution from the coral $\delta^{18}O$ (McCulloch et al. 1994; Gagan et al. 1998):

$$\Delta\delta^{18}O = d\delta^{18}O/dT \times [T_{\delta^{18}O} - T_{Sr/Ca}],$$

where $d\delta^{18}O/dT$ is the slope of −0.18 ‰ per °C derived for *Porites* sp. (Gagan et al. 1998), and the Sr/Ca–SST relationship is taken from McCulloch et al. (1994; and see also Calvo et al. 2007).

Climatic variables

Recent in situ climatic data from the study site are not available, so data recorded at nearby stations were used in this study. The annual SST records from 1937 to 2009 were calculated by averaging the monthly SST, extracted from the HadISST1.1 dataset (Rayner et al. 2003; http://badc.nerc.ac.uk/view/badc.nerc.ac.uk__ATOM__dataent_hadisst) on a 1° × 1° grid centered on 16.5°S, 146.5°E (~45 km from the sampling sites). Annual rainfall totals for the period 1943–2009 were calculated from the monthly rainfall data recorded at the Cairns Aero Weather Station (16.87°S, 145.75°E; ~46 km from the sampling site; http://www.bom.gov.au/climate/data/?ref=ftr).

Spectral analysis

To identify any low-frequency cycles within the climate associated coral records, red noise spectral analysis was performed on the coral geochemical series using the program REDFIT (Schulz and Mudelsee 2002).

Results

Geochemical records and growth rates

The results of the geochemical analysis (Sr/Ca, Mg/Ca, $\delta^{18}O$, $\delta^{13}C$, and $\Delta\delta^{18}O$) and growth rate of the two coral samples are shown in Fig. 3 and Table 1.

The mean Sr/Ca values for cores 10AR1 and 10AR2 were 8.857 ± 0.038 (1σ) and 9.031 ± 0.042 (1σ) mmol mol^{-1}, respectively (Table 1). The difference between the two means is 0.174 mmol mol^{-1}, which is statistically significant ($t = -25.9$, $df = 142$, $p < 0.001$) and outside the range of analytical error. The amplitudes of the total variations in Sr/Ca ratios were 0.231 and 0.175 mmol mol^{-1} for 10AR1 and 10AR2, respectively (Table 1). The two Sr/Ca time series are significantly but weakly correlated ($r = 0.26$, $n = 71$, $p = 0.01$; Fig. 3b).

The mean Mg/Ca values of 10AR1 and 10AR2 between the 1930s and 2009 differ by 0.663 mmol mol^{-1} (10AR1 = 4.256 ± 0.211 mmol mol^{-1}, 1σ; 10AR2 = 3.59 ± 0.170 mmol mol^{-1}, 1σ; Table 1). This difference is also statistically significant ($t = 20.8$, $df = 142$, $p < 0.001$) and outside the range of analytical error. The variation in the Mg/Ca ratios of 10AR2 is up to 0.704 mmol mol^{-1} in amplitude and is a little smaller than 0.991 mmol mol^{-1} of 10AR1 (Table 1). As with the intercoral Sr/Ca records, the variations of the two Mg/Ca series are not significantly correlated ($r = -0.07$, $n = 71$, $p = 0.28$; Fig. 3d).

The overall mean $\delta^{18}O$ of 10AR1 (−4.43 ± 0.18 ‰, 1σ) and 10AR2 (−4.76 ± 0.20 ‰, 1σ) differs by 0.33 ‰ (Table 1), which is also statistically significant ($t = 10.3$, $df = 142$, $p < 0.001$) and outside the range of analytical error. The amplitudes of their variation are also different: 0.90 ‰ for 10AR1 and 1.16 ‰ for 10AR2 (Table 1). However, the covariations between the two coral $\delta^{18}O$ series are significant, though the correlation is weak ($r = 0.42$, $n = 71$, $p < 0.001$; Fig. 3f).

The difference of the two corals' mean $\delta^{13}C$ values (10AR1: −2.13 ± 0.47 ‰, 1σ; 10AR2: −2.27 ± 0.54 ‰, 1σ; Table 1) is not statistically significant ($t = 1.59$, $df = 142$, $p = 0.12$) and is within the analytical error. The amplitude of the variation of $\delta^{13}C$ of 10AR1 (1.67 ‰) was smaller than that of 10AR2 (2.13 ‰; Table 1), which is a similar relationship to that seen in the $\delta^{18}O$ signature.

The mean $\Delta\delta^{18}O$ values obtained from the two corals were significantly different ($t = 26.9$, $df = 142$, $p < 0.001$) at 0.54 ± 0.20 ‰ (1σ) for 10AR1 and −0.33 ± 0.19 ‰ (1σ) for 10AR2 (Table 1). However, the amplitudes of the variation of the two $\Delta\delta^{18}O$ series were very close at 0.85 and 0.89 ‰ for 10AR1 and 10AR2, respectively (Table 1). The two $\Delta\delta^{18}O$ series are significantly but weakly correlated ($r = 0.38$, $n = 71$, $p < 0.001$; Fig. 3j).

Calculated from the annual growth rate results, the means for 10AR1 and 10AR2 were 13.0 ± 1.9 and 16.0 ± 1.1 mm yr^{-1}, respectively (Table 1); the difference is statistically significant ($t = -11.4$, $df = 142$, $p < 0.001$).

Comparisons of coral geochemical records and climatic variables

The annual resolution Sr/Ca, $\delta^{18}O$, and $\Delta\delta^{18}O$ series are compared with climatic variables as their climatic and environmental significance is more straightforward than Mg/Ca and $\delta^{13}C$. The correlation between Sr/Ca and SST in 10AR2 ($r = -0.67$, $n = 73$, $p < 0.0000001$; Fig. 4d) is much better than that in 10AR1 ($r = -0.20$, $n = 71$, $p = 0.05$; Fig. 4b). Correspondingly, the variations of Sr/Ca in 10AR2 are much closer to that of SST than in 10AR1 (Fig. 4a, c). The correlations and variations between the $\delta^{18}O$ and SST for both 10AR1 and 10AR2 were similar (10AR1: $r = -0.41$, $n = 71$, $p = 0.0002$; Fig. 4e, f;

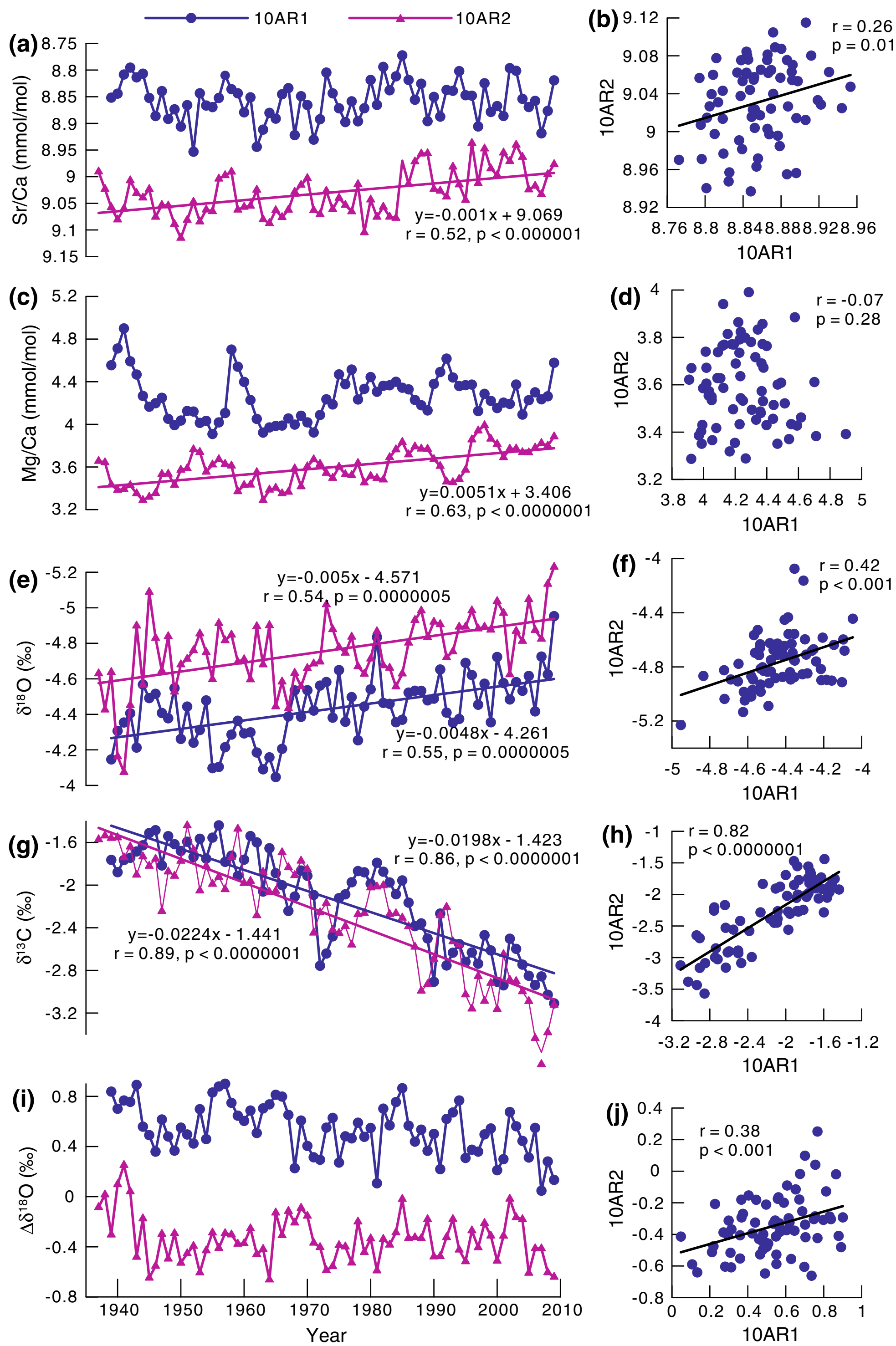

Fig. 3 Comparisons of geochemical records from the two coral samples. The five figures in the *left panel* show the temporal variations of annual resolution series from the two *Porites* sp. corals 10AR1 (*blue lines with solid circles*) and 10AR2 (*red lines with solid triangles*) for **a** Sr/Ca, **c** Mg/Ca, **e** $\delta^{18}O$, **g** $\delta^{13}C$, and **i** $\Delta\delta^{18}O$. *Blue* and *red solid lines* show the long-term trends in the geochemistry of 10AR1 and 10AR2, respectively. Only those trends that are significant are shown by *regression lines*. The five figures in *right panel* show the correlations of corresponding geochemical records of 10AR1 and 10AR2 in the figures in the *left panel* for **b** Sr/Ca, **d** Mg/Ca, **f** $\delta^{18}O$, **h** $\delta^{13}C$, and **j** $\Delta\delta^{18}O$. The significant correlations are shown by regression lines

10AR2: $r = -0.40$, $n = 73$, $p = 0.0002$; Fig. 4g, h). As with the correlation between Sr/Ca and SST, the correlation and covariation between $\Delta\delta^{18}O$ from 10AR2 and rainfall ($r = -0.34$, $n = 67$, $p < 0.01$; Fig. 4k, l) is also better than that between $\Delta\delta^{18}O$ from 10AR1 and rainfall ($r = -0.19$, $n = 67$, $p = 0.06$; Fig. 4i, j).

Discussion

Coral geochemical records and growth rates

The Sr/Ca ratios of 10AR2 show a gradual decline from the 1930s to 2009 (Fig. 3a), which suggests a rise in SST since

Table 1 Summary of geochemical data and growth rate for corals 10AR1 and 10AR2

	Mean values						Amplitudes					
	Sr/Ca	Mg/Ca	$\delta^{18}O$	$\delta^{13}C$	$\Delta\delta^{18}O$	Growth rate	Sr/Ca	Mg/Ca	$\delta^{18}O$	$\delta^{13}C$	$\Delta\delta^{18}O$	Growth rate
10AR1	8.857	4.256	−4.43	−2.13	0.54	13.0	0.231	0.991	0.90	1.67	0.85	7.0
10AR2	9.031	3.593	−4.76	−2.27	−0.33	16.0	0.175	0.704	1.16	2.13	0.89	4.0

Amplitudes are calculated as the difference between the maximum and minimum geochemical values. Isotope values are reported in ‰ VPDB, elemental ratios are reported in mmol mol^{-1}, and growth rate is reported in mm yr^{-1}. The coral life spans are 1937–2009 for 10AR1 and 1939–2009 for 10AR2

the 1930s as Sr/Ca is inversely related to SST (Smith et al. 1979; Beck et al. 1992). However, this trend does not appear in Sr/Ca series from 10AR1 (Fig. 3a).

Different from Sr/Ca, the Mg/Ca ratios of 10AR2 show a gradual rising trend from the 1930s onwards (Fig. 3c). As Mg/Ca is positively correlated with SST (Mitsuguchi et al. 1996, 2003), this rising trend may record the increase in SST from the 1930s. In contrast, the Mg/Ca series obtained from 10AR1 has no secular rising or declining trend from the 1930s (Fig. 3c).

As with the Sr/Ca series, both $\delta^{18}O$ time series have followed a decreasing trend since the 1930s (Fig. 3e). The similarity of their secular decreasing trends may also indicate an increase in SST from the 1930s because coral $\delta^{18}O$ is partly temperature dependent (Swart and Coleman 1980; Dunbar and Wellington 1981). Both coral $\delta^{13}C$ time series show a continuously decreasing trend since the 1930s, and their correlation is high ($r = 0.82$, $n = 71$, $p < 0.0000001$, Fig. 3g, h). This decrease can be attributed to the addition of anthropogenic CO_2 emissions to the atmosphere; i.e., the ^{13}C Suess effect, which affects almost all long coral $\delta^{13}C$ records (Swart et al. 2010; Al-Rousan and Felis 2013). As a proxy of seawater $\delta^{18}O$, both coral $\Delta\delta^{18}O$ values do not show a significant long-term trend (Fig. 3i), which suggests the variations of surrounding seawater $\delta^{18}O$ are not linear since the 1930s.

The significant difference in growth rates of two coral suggests that 10AR2 grew more quickly and more consistently than 10AR1. Both the Sr/Ca and Mg/Ca ratios of 10AR2 are correlated well with the annual growth rates, whereas the same correlations in 10AR1 are poor (Fig. 5a, b, e, f). This may suggest that the geochemical variables preserved in 10AR1 have suffered from vital effects, such as the influence of calcification rate or the activity of symbionts on the response to SST (Cohen et al. 2002). However, such vital effects appear to have been relatively weak for 10AR2. As shown by the X-rays in Fig. 2, the annual bands in 10AR1 are not very clear, and the orientation of the main growth axis is variable. In contrast, the quality of 10AR2 is much better than that of 10AR1 (Fig. 2). The good correlations of $\delta^{13}C$ and $\delta^{18}O$ with the annual growth rates in both corals suggest the strong influence of annual growth rate on isotopic composition (Fig. 5c, d, g, h; McConnaughey 1989). Such close correlation between annual variations of coral $\delta^{13}C$ and $\delta^{18}O$ is common (Lough 2004).

Relationships between intracoral geochemical records

The Sr/Ca and Mg/Ca ratios of 10AR1 are significantly but weakly correlated ($r = -0.48$, $n = 71$, $p < 0.0001$; Fig. 6a). However, their correlations with $\delta^{18}O$ are not significant (for Mg/Ca and $\delta^{18}O$, $r = -0.22$, $n = 71$, $p = 0.03$, Fig. 6b; for Sr/Ca and $\delta^{18}O$, $r = 0.12$, $n = 71$, $p = 0.16$, Fig. 6c;). In contrast, these three ratio series from 10AR2 are significantly correlated with each other (for Sr/Ca and Mg/Ca, $r = -0.60$, $n = 73$, $p < 0.$ 0000001, Fig. 6f; for Mg/Ca and $\delta^{18}O$, $r = -0.45$, $n = 73$, $p < 0.0001$, Fig. 6g; for Sr/Ca and $\delta^{18}O$, $r = 0.43$, $n = 73$, $p < 0.001$, Fig. 6h). Coral Sr/Ca, Mg/Ca, and $\delta^{18}O$ are usually correlated with each other, because all may respond to variations in SST, although to differing extents (Cardinal et al. 2001; Watanabe et al. 2001b; Quinn and Sampson 2002; Mitsuguchi et al. 2003; Yu et al. 2005; Hetzinger et al. 2006; Montagna et al. 2007).

The significant correlations occur between $\delta^{13}C$ and $\delta^{18}O$ in two corals (10AR1: $r = 0.56$, $n = 71$, $p < 0.0000001$, Fig. 6d; 10AR2: $r = 0.59$, $n = 73$, $p < 0.0000001$, Fig. 6i). These linear correlations between skeletal $\delta^{13}C$ and $\delta^{18}O$ are common in biological carbonates such as coral showing the strong kinetic disequilibrium effects during their growth (McConnaughey 1989).

The $\delta^{18}O$ and $\Delta\delta^{18}O$ series are also correlated well (10AR1: $r = 0.81$, $n = 71$, $p < 0.0000001$, Fig. 6e; 10AR2: $r = 0.76$, $n = 73$, $p < 0.0000001$, Fig. 6j) in both 10AR1 and 10AR2. Coral $\delta^{18}O$ is mainly controlled by both SST and ambient seawater $\delta^{18}O$ (Swart and Coleman 1980; Dunbar and Wellington 1981), and coral $\Delta\delta^{18}O$ represents the $\delta^{18}O$ levels in the surrounding seawater (McCulloch et al. 1994; Gagan et al. 1998). Therefore, this correlation may indicate that the annual resolution coral $\delta^{18}O$ series is primarily controlled by changes in seawater $\delta^{18}O$ rather than temperature in the study area.

Possible impacts on the offset of intercoral geochemical records

Based on the above intercoral comparisons, the annual resolution geochemical records obtained from the two

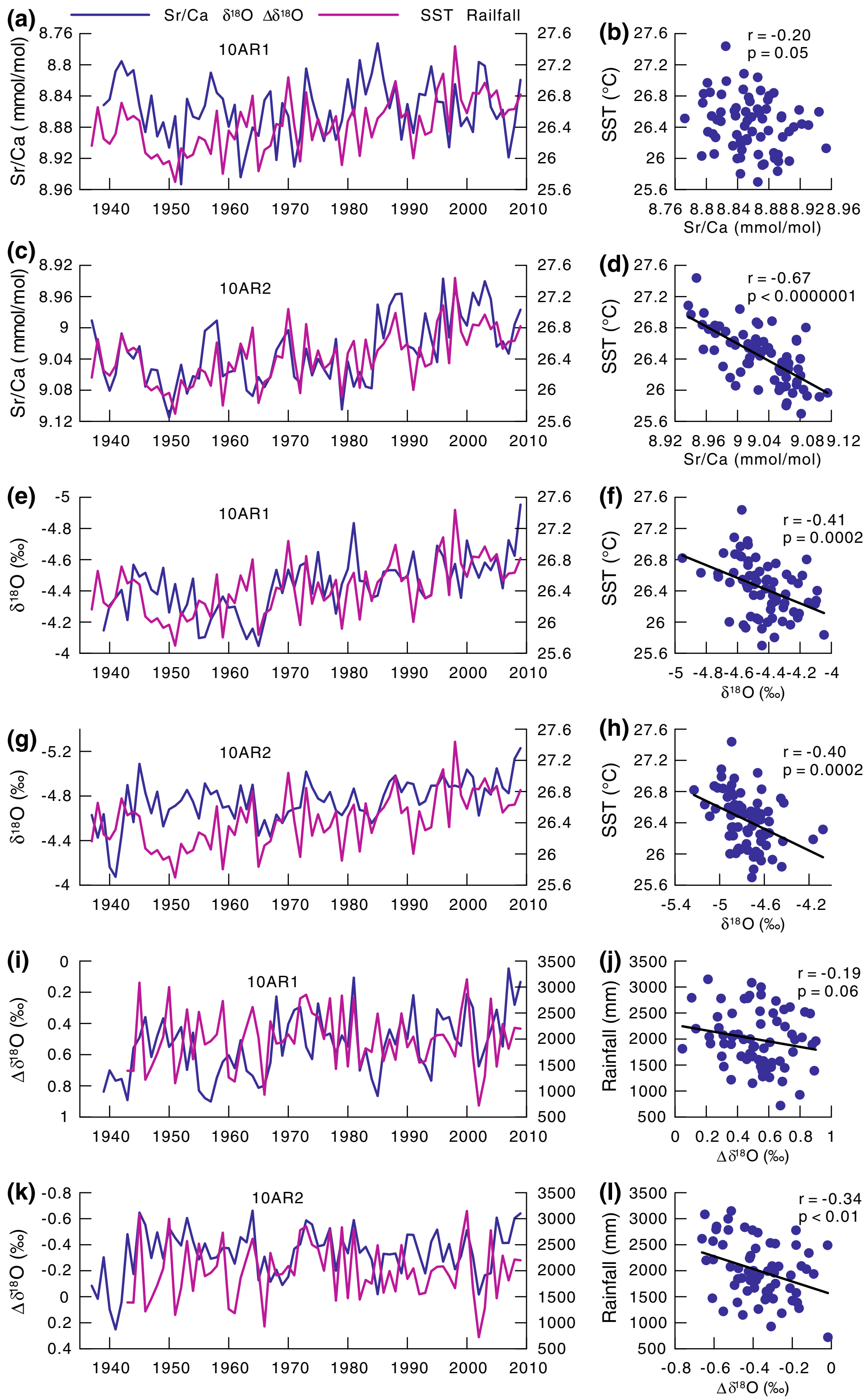

Fig. 4 Relationships between coral geochemistry and climatic variables. The six figures in the *left panel* show the temporal variations of annually resolved Sr/Ca, δ^{18}O, and $\Delta\delta^{18}$O (*blue lines*) from the two *Porites* sp. corals: 10AR1 (**a, e, i**) and 10AR2 (**c, g, k**), along with annual SST and rainfall (*red lines*). The six figures in the *right panel* show the correlations between corresponding coral geochemical and climate records. The correlations that are significant are shown by regression lines. **b, d** Sr/Ca and SST, **f, h** δ^{18}O and SST, **j, l** $\Delta\delta^{18}$O and rainfall

corals are not particularly well replicated. Although most of the same geochemical series of the two corals follow similar trends and have significant correlations (Fig. 3), their absolute values, and the amplitude of their variability, show differences that may be controlled by physiological factors such as growth rate. Many high-resolution studies have demonstrated that growth rate has a significant effect on elemental and isotopic ratios in the same colony, and

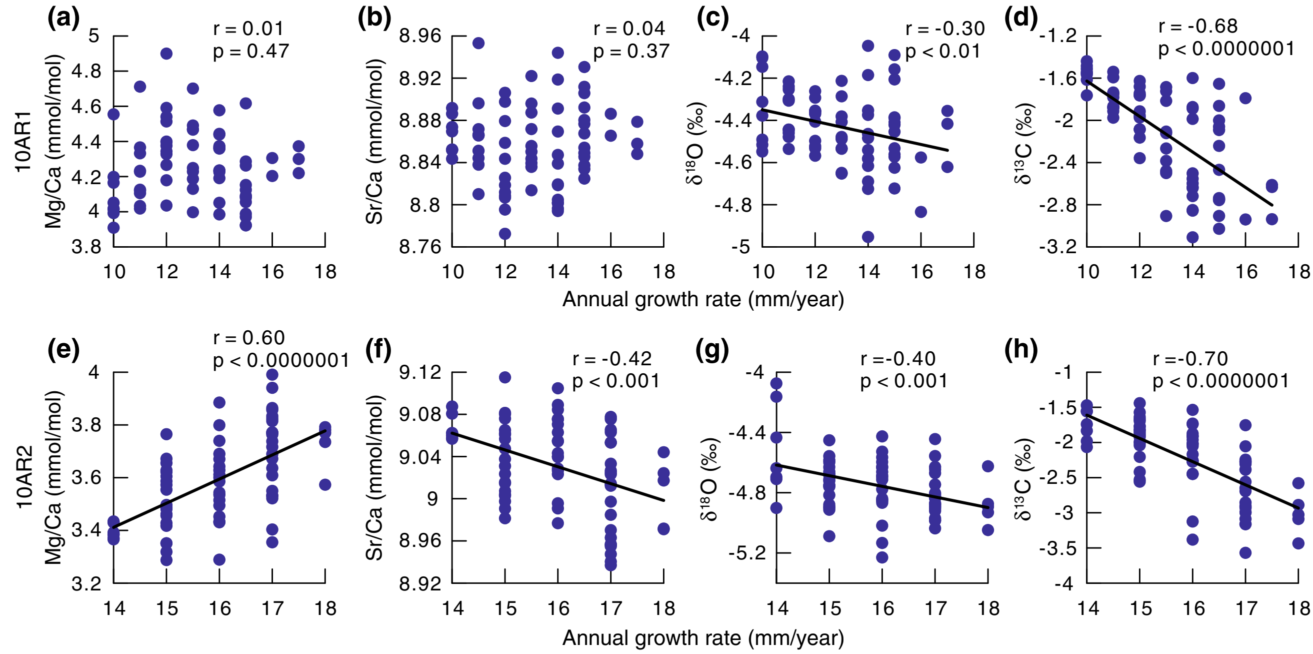

Fig. 5 Relationships between annual growth rate of the two *Porites* sp. corals 10AR1 (*upper panel*) and 10AR2 (*lower panel*) and annually resolved geochemical records: **a**, **e** Mg/Ca and growth rate, **b**, **f** Sr/Ca and growth rate, **c**, **g** $\delta^{18}O$ and growth rate, **d**, **h** $\delta^{13}C$ and growth rate. The correlations that are significant are shown by regression lines

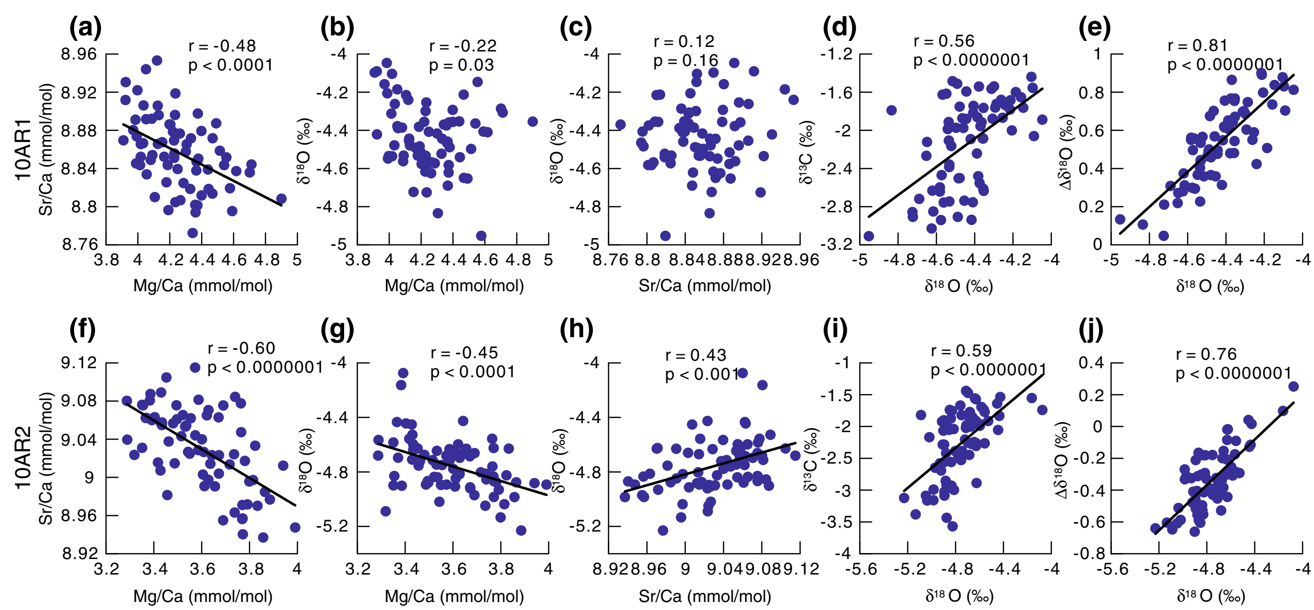

Fig. 6 Relationships between intracoral geochemical records of the two *Porites* sp. corals 10AR1 (*upper panel*) and 10AR2 (*lower panel*) comparing **a**, **f** Sr/Ca and Mg/Ca, **b**, **g** $\delta^{18}O$ and Mg/Ca, **c**, **h** $\delta^{18}O$ and Sr/Ca, **d**, **i** $\delta^{13}C$ and $\delta^{18}O$, and **e**, **j** $\Delta\delta^{18}O$ and $\delta^{18}O$. The correlations that are significant are shown by regression lines

even in the same corallite, for almost all kinds of scleractinian corals (e.g., Weber 1973; McConnaughey 1989; de Villiers et al. 1994, 1995; Watanabe et al. 2002; Felis et al. 2003; Mitsuguchi et al. 2003; Goodkin et al. 2005). Furthermore, the growth rate of *Porites* sp. coral shows considerable variability between corals living at similar locations (Lough and Barnes 2000). Therefore, the significant differences in growth rate may contribute to the differences observed between the geochemical proxies from the two corals.

In general, the Sr/Ca ratios of a slow-growing skeleton tend to be higher than those of a fast-growing skeleton at the same temperature (Weber 1973; de Villiers et al. 1995; Alibert and McCulloch 1997; Goodkin et al. 2005). Here, the opposite behavior is seen, with the mean Sr/Ca value of the slow-growing 10AR1 being much lower than that of the relatively fast-growing 10AR2, which suggests the influence of other vital effects, such as algal symbionts affecting the uptake of Sr into the coral skeleton (Cohen et al. 2002).

The relatively fast-growing 10AR2 has a lower mean value of Mg/Ca than the slow-growing 10AR1, which is also contrary to previous studies of *Porites* corals that were based on bulk samples from different colonies (Inoue et al. 2007), and suggests that the Mg/Ca offset may also be caused by biological/metabolic differences between the two colonies (Quinn and Sampson 2002; Fallon et al. 2003; Mitsuguchi et al. 2003; Meibom et al. 2004) and/or the loss of Mg during chemical treatment of the coral skeleton (Mitsuguchi et al. 2001; Watanabe et al. 2001a). The two corals were treated using the same chemical protocols, but they may have different Mg distributions induced by the differing biological controls on each of them. Therefore, the same chemical treatment may still lead to the observed differences in the Mg/Ca series.

The mean values of both $\delta^{13}C$ and $\delta^{18}O$ from 10AR1 were slightly more positive than those from 10AR2. This may be because most intercolony differences in mean coral isotope signatures are related to growth rate, as this may influence the kinetic isotope disequilibrium effect (McConnaughey 1989; Felis et al. 2003).

The value of $\Delta\delta^{18}O$ is calculated from the $\delta^{18}O$ and Sr/Ca ratios, so its variation is largely controlled by these two variables. The external hydrographic conditions that the two corals experienced should be similar, so their distinctly different mean $\Delta\delta^{18}O$ values may be attributed to their different mean $\delta^{18}O$ and Sr/Ca ratios as described above.

In summary, the correlations of the stable isotopic ratios (i.e., $\delta^{18}O$ and $\delta^{13}C$) are more statistically significant than those of the elemental ratios (i.e., Sr/Ca and Mg/Ca) between these two corals, which suggests that the elemental ratios are more susceptible to biological/metabolic effects than are the isotopic compositions.

Relationship between coral geochemistry and climatic variables

As the factors controlling Mg/Ca and $\delta^{13}C$ in corals remain to be fully quantified (McConnaughey 1989; Swart et al. 1996; McConnaughey et al. 1997; McConnaughey 2003; Mitsuguchi et al. 2003; Meibom et al. 2004), their climatic significance will not be discussed here. Instead, we focus on the annual resolution Sr/Ca, $\delta^{18}O$, and $\Delta\delta^{18}O$ series as their climatic and environmental significance is more straightforward. Even so, it is probable that the long-term increasing trends in the Mg/Ca series of both corals partly reflect variations in SST since the 1930s, and the continuously decreasing trend in the two $\delta^{13}C$ series reflects the changing $\delta^{13}C$ composition related to fossil fuel burning (i.e., the Suess effect).

We calibrated the Sr/Ca ratios of 10AR2 with the annual SSTs as Sr/Ca is widely used to reconstruct past SST records and the correlation between Sr/Ca and SST in 10AR2 is much better than that in 10AR1 (Fig. 4a–d). The relationship between Sr/Ca and SST in 10AR2 obtained by a linear least squares regression is shown below.

$$\mathrm{Sr/Ca} \times 10^3 = 11.209 - 0.0824 \times \mathrm{SST}$$

The intercept (A) and slope (B) values are very different to the previous Sr/Ca–SST relationships generated from high-resolution coral series in which the values generally range from 9.760 to 10.956, and from −0.0393 to −0.0795 for A and B, respectively (Wei et al. 2007). Despite these differences, a good linear regression line can be obtained when plotting A against B of the thermometer by annual calibration and other ones by monthly calibration compiled by Wei et al. (Wei et al. 2007; Fig. 7). This method was suggested by Marshall and McCulloch (2002) to check the validity of Sr/Ca–SST calibration and was based on the hypothesis that corals from different localities around the world are responding to their own particular environment, or that certain types of environments exert a control on coral physiology. Therefore, the excellent linear relationship shown in Fig. 7 suggests that the annual calibration of Sr/Ca–SST supports this hypothesis and that the use of annual resolution Sr/Ca series as a proxy for SST in this study may be reliable.

It is worth noting that this calibration is almost identical to the modified Sr/Ca–SST equation used to model annual mean SST by Gagan et al. (2012). Both the slope (−0.0824) and intercept (11.209) of our equation are very close to those of their equation (−0.084 and 11.278, respectively, Fig. 7). The equation of Gagan et al. (2012) corrects for the attenuation effect inherent within the geochemical records and is believed to provide accurate annual mean SST records (Gagan et al. 2012). It is reasonable to assume that data obtained from corals analyzed using an annual sampling resolution incorporates all of the significant seasonal factors, and any seasonality inherent within the climatic and environmental signals has been averaged out. As a result, the attenuation effects induced by differences in seasonal growth appear to be negligible when calibrating these Sr/Ca ratios with annual instrumental SST records. However, the detailed procedures best used for this calibration require further investigation. The agreement of our Sr/Ca–SST equation with that of Gagan

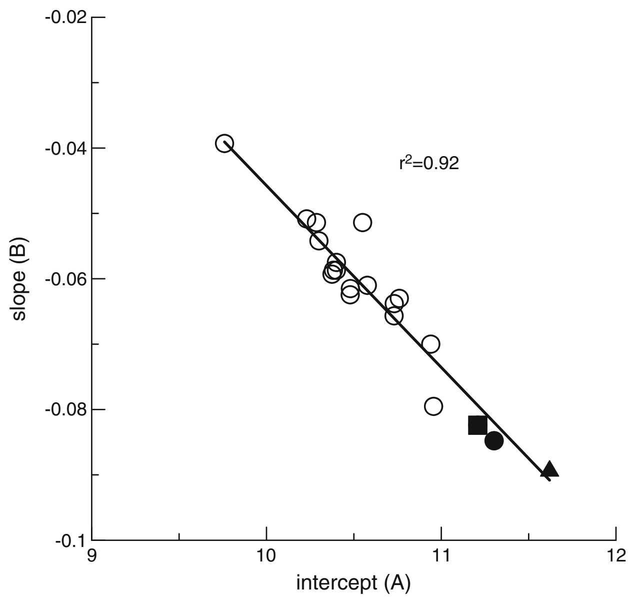

Fig. 7 Plot of slope (B) against intercept (A) for the selected Sr/Ca–SST calibrations. Sr/Ca–SST calibrations are expressed as Sr/Ca = A + B × SST. The *solid square* indicates annually resolved calibration of the *Porites* sp. coral 10AR2 from Arlington Reef (this study). The *solid circle* indicates the mean annual calibration on the *Porites* sp. corals from other locations (Gagan et al. 2012), and the *solid triangle* indicates seawater. The *open circles* indicate monthly resolution calibrations from Marshall and McCulloch (2002) and Wei et al. (2007)

et al. (2012) again indicates that our calibration is reliable and that it can be applied to annual mean SST reconstruction on the GBR.

The similar correlations between the δ^{18}O and SST for both 10AR1 and 10AR2 (Fig. 4e–h) indicate that coral δ^{18}O is affected by both SST and ambient seawater δ^{18}O (Swart and Coleman 1980; Dunbar and Wellington 1981). The annual resolution coral δ^{18}O series appears to be primarily controlled by changes in seawater δ^{18}O rather than temperature (see text in section "Discussion": Relationships between intracoral geochemical records), so its correlation with SST was not significant for either coral. Even so, the δ^{18}O–SST sensitivities (−0.21 ‰ °C^{-1} for 10AR1 and −0.229 ‰ °C^{-1} for 10AR2) are close to the empirically calibrated sensitivity range; i.e., −0.08 to −0.22 ‰ °C^{-1} (Gagan et al. 2012). The sensitivity for the faster growing 10AR2 is very close to −0.23 ‰ °C^{-1}, which is the theoretical maximum of δ^{18}O–SST sensitivity in biogenic aragonite indicated by the model of Gagan et al. (2012). This again suggests that the attenuation effect put forward by Gagan et al. (2012) could be corrected for by annual calibration.

Coral $\Delta\delta^{18}$O reflects changes in the δ^{18}O of the surrounding seawater, and so, can also provide information regarding rainfall amounts (McCulloch et al. 1994; Shen et al. 2005; Deng et al. 2009). Therefore, the $\Delta\delta^{18}$O series from 10AR2 records, the most characteristic variations in rainfall since 1943 as the correlation between $\Delta\delta^{18}$O from 10AR2 and rainfall, is better than that between $\Delta\delta^{18}$O from 10AR1 and rainfall (Fig. 4i–l). However, it is difficult to establish a quantitative relationship between coral $\Delta\delta^{18}$O and rainfall, especially as it is likely that the δ^{18}O of the surrounding seawater is also affected by evaporation. In this respect, the annual resolution coral $\Delta\delta^{18}$O series represents a proxy for annual variations in sea surface salinity (SSS), which is largely controlled by the balance between precipitation and evaporation (Delcroix et al. 1996). It is notable that the amplitude of the variations in the two coral $\Delta\delta^{18}$O series is nearly the same (Table 1) and that the correlation is weak (Fig. 3). This indicates that the coral $\Delta\delta^{18}$O values may be used to indicate the amplitude of variations in SSS from the 1930s to 2009 in the study area.

The results of red noise spectral analysis suggest the presence of robust decadal periodicities of around 16 yr in the annual resolution Sr/Ca and $\Delta\delta^{18}$O time series from 10AR2 (Fig. 8). The low-frequency variability agrees with the observation that SST and rainfall across the GBR and northeast Australia generally exhibit decadal variability closely linked to the activity of the IPO (Lough 1994; Power et al. 1999; Arblaster et al. 2002; Verdon et al. 2004; Calvo et al. 2007; Lough 2007; Rodriguez-Ramirez et al. 2014). Interannual cycles, with periods of around 2–3 yr, are also evident within the annual resolution Sr/Ca and $\Delta\delta^{18}$O series from 10AR2 (Fig. 8), and probably represent the El Niño-Southern Oscillation signature.

Climatic significance of the annual resolution coral records

The relationships outlined above between geochemistry and climate suggest that 10AR2 is an ideal coral to record annual climate variability, but that 10AR1 is less suitable for annual paleoclimate reconstruction. Such differences between two corals are understandable because non-climatic factors may affect the fidelity of the coral record such that some may have no climatic significance at all (Lough 2004). As for this study, the geochemical records from 10AR1 may be affected more seriously than those from 10AR2 by non-climatic factors such as growth rate, calcification rate, and symbiont activity, even though the external climatic and hydrographic conditions they experienced should have been the same. It is notable that while the geochemical records from 10AR2 are closely correlated with annual growth rates, they still record climatic change well, which suggests that the climatic significance of faster and steadier growing coral is independent of skeletal growth rate (Mitsuguchi et al. 2003; Jones et al. 2009). Therefore, such annual resolution coral records offer a potential approach to reconstructing past climate change (Dunbar et al. 1994; Cole et al. 2000; Zinke et al. 2014). This is especially the case for research into climate change

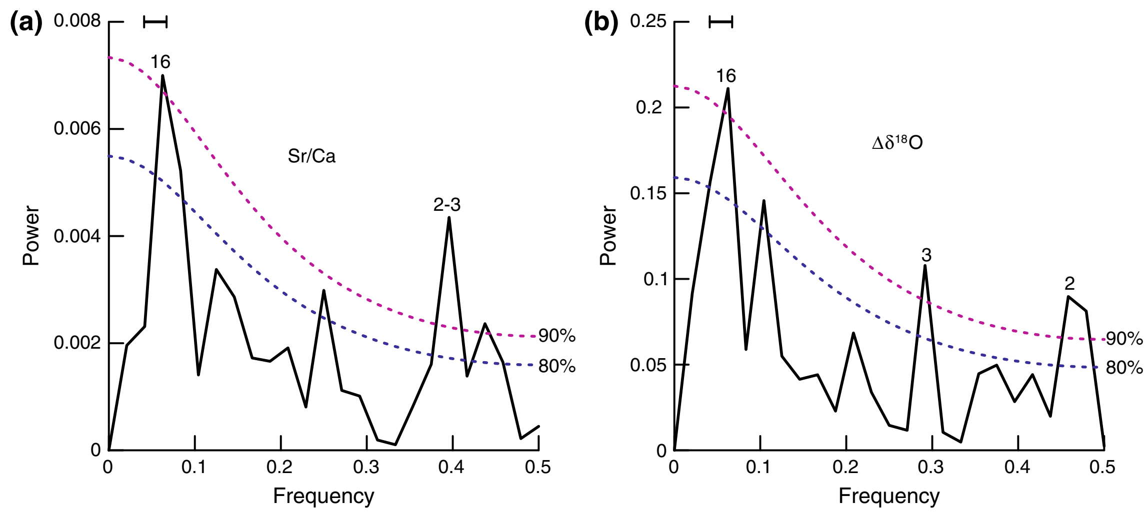

Fig. 8 Power spectra of **a** Sr/Ca and **b** $\Delta\delta^{18}O$ from 10AR2 calculated using the software REDFIT (Schulz and Mudelsee 2002). The *horizontal bars* indicate the bandwidths, and the *dashed lines* indicate the 90 and 80 % confidence levels

over long timescales, in which annual resolution sampling can save much time and expense, but still provides similar information to studies based on high-resolution sampling. However, some important issues must be addressed when considering the use of annual resolution coral geochemical records in this field. First, the use of samples obtained from fast and steadily growing coral with a stable maximum growth axis is preferable. For example, coral samples such as 10AR2 are acceptable, while 10AR1 was not suitable. Second, replication from different coral colonies is very important as suggested and demonstrated in several recent studies (Lough 2004; DeLong et al. 2013; Zinke et al. 2014). Ideally, at least 2–3 coral cores from a reef location are necessary because coral records extracted from a single coral colony cannot be used to distinguish between climate signals and biologically induced noise. For those aiming to study long timescale climate variability, the analytical burden of 2–3 replications at an annual sampling interval is still less than that of a single core at a monthly sampling resolution, and regardless of this, replication is essential.

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